

Suspension Polymerization Behavior of Styrene under Stirring with Unsteady Speed Impeller

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Effects of unsteady rate stirring mode on the particle size and the size distribution were thoroughly investigated in the preparation of cross-linked polystyrene resins under suspension polymerization conditions. Thus, unsteady rate stirring generally gave polystyrene resins in smaller size and narrower distribution with comparison to the usual steady rate stirring under same conditions other than the stirring mode. Especially, unsteady rate mode can give monodispersed polystyrene-divinylbenzene copolymer beads.

Key words: suspension polymerization, polystyrene, unsteady rate stirring, monodispersed resins

1. INTRODUCTION

Suspension polymerization is an important technology for preparing industrial materials, such as various vinyl polymers. Some modificational efforts have been continuously done to control the size and the size distribution of resin particles aiming at producing high grade plastics. Some recent articles have reported that the size distribution can become controllable by adjusting the viscosity of the continuous phase, the choice of stabilizers and the stirring rate [1-3]. Few articles, however, should focus on the importance of the mode of stirring to the size distribution [4-5].

Recently, we have proposed some new solid supports having order-made functionalities for specific solid phase organic syntheses (SPOS) [6]. The solid supports used in the studies were cross-linked polystyrene resins with some specific functional groups, which were prepared by radical suspension polymerization. Hence, we found that the size distribution of the resins showed a significant influence on their availability and effectiveness in actual use in SPOS. Thus, we were stimulated to investigate on a convenient and effective procedure to get a resin particles of narrow size distribution by an introduction of unsteady impelling.

2. EXPERIMENTAL

2.1 Materials

Benzoyl peroxide (BPO) was purchased from Aldrich Chemical Japan, Co. Ltd. and was used without further purification. Poly(vinyl alcohol) (PVA, $DP_n \approx 2000$) was purchased from Tokyo Kasei Kogyo Co. Ltd. All other chemicals and solvents were obtained from Wako Co. Ltd. and were used without further purification.

2.2 Preparation of chloromethyl resin

Chloromethyl resin was prepared by the similar procedure to the reported method [7]. A solution of acacia gum (8.0 g) and NaCl (5.0 g) in water (200 ml) was placed in a 500 ml round bottomed flask equipped with a polytetrafluoroethylene (PTFE) impeller. After

N_2 bubbling for 2 h, a solution of styrene (9.72 mL, 0.085 mol), 4-vinylbenzyl chloride (1.93 mL, 0.014 mol), divinylbenzene (DVB) (0.28 mL, 2.0 mmol) and BPO (0.171 g, 0.71 mmol) in chlorobenzene (11.4 ml) was added to the aqueous solution with stirring. The reaction mixture was stirred at 250 rpm by the unsteady speed impeller at 85 °C for 20 h. The resins obtained were filtered off and washed with hot water. Then the resin was washed with tetrahydrofuran (THF) using a Soxhlet extractor for 24 h. Residual resins were recovered and washed again with diethyl ether and hexane, successively. The resin was dried *in vacuo* at ambient temperature for 24 h (8.79 g, 81 % yield) and sieved out by six classes of the sieves of 500, 355, 212, 150, 75, and 45 μm as following: range of the size (yield, %-fraction), $\sim 500 \mu\text{m}$ (0.10 g, 1 %), 500~355 μm (0.28 g, 3 %), 355~212 μm (5.92 g, 67 %), 212~150 μm (1.79 g, 20 %), 150~75 μm (0.55 g, 6 %), 75~45 μm (0.03 g, 0 %), 45 μm ~ (0 g, 0 %). The agitation speed was changed from 200 rpm to 400 rpm by the impeller of unsteady speed and steady speed modes, and examined by the same procedure to evaluate the resin size and size distribution.

2.3 Preparation of polystyrene resin

Polystyrene resins were prepared by the similar procedure to chloromethyl resins described above; styrene (11.73 mL, 0.10 mol), DVB (0.28 mL, 2.0 mmol), and BPO (0.171 g, 0.71 mmol) in chlorobenzene (11.4 mL) were the organic phase. The agitation speed was changed from 200 rpm to 400 rpm by the impeller of unsteady speed and steady speed modes, and examined by the same procedure to evaluate the resin size and size distribution.

2.4 Preparation of polystyrene resin using PVA and tribasic calcium phosphate (TCP)

A solution of PVA (0.01 g) and TCP (0.1 g) in water (200 mL), was placed in a 500 ml round bottom flask equipped with a PTFE impeller. After N_2 bubbling for 2 h, a solution of styrene (11.73 mL, 0.10 mol), DVB

(0.28 mL, 2.0 mmol) and BPO (0.171 g, 0.71 mmol) was added to the aqueous solution with stirring. The reaction mixture was stirred at 200 rpm by the unsteady speed impeller at 85 °C for 20 h.

The resins obtained were filtered off and washed with hot water. Then the resin was washed with THF using a Soxhlet extractor for 24 h. Residual resins were recovered and washed again with diethyl ether and hexane, successively. The resin was dried *in vacuo* at ambient temperature for 24 h (9.29 g, 90 % yield) and sieved out by six classes of the sieves of 500, 355, 212, 150, 75, and 45 μm as following: range of the size (yield, %-fraction), $\sim 500 \mu\text{m}$ (0.37 g, 4 %) 500~355 μm (0.78 g, 7 %), 355~212 μm (7.46 g, 80 %), 212~150 μm (0.61 g, 7 %), 150~75 μm (0.11 g, 1 %), 75~45 μm (0 g, 0 %), 45 μm ~ (0 g, 0 %). The agitation speed was changed from 200 rpm to 400 rpm by the impeller of unsteady speed and steady speed modes, and examined by the same procedure to evaluate the resin size and size distribution.

2.5 Unsteady speed impeller

The stirrer with unsteady speed impeller used here was a ULCAM UL-MIX NCG-001. The impeller can control the stirring rate between twice and half of the centered rate by a program. Details of the programmed rotational rate controlling is explained in the literature [8].

3. RESULTS AND DISCUSSIONS

3.1 Particle size distribution of chloromethyl resin

Chloromethyl resin is a terpolymer from styrene - divinylbenzene (DVB) - 4-chloromethylstyrene (CMB). Summary of the typical conditions of the suspension polymerization in chlorobenzene is described in Table I. The viscosity of the continuous phase is controlled by adding acacia gum.

Table I Recipe for preparation of chloromethyl resin

| | |
|-----------------|---------------------|
| Water | 200 mL |
| Chlorobenzene | 11.4 mL |
| Styrene | 9.72 mL (0.085 mol) |
| DVB | 0.28mL (2.0 mmol) |
| CMS | 1.93 mL (0.014 mol) |
| BPO | 0.171 g (0.71 mmol) |
| Acacia gum | 8.0 g |
| NaCl | 5.0 g |
| Temperature | 85°C |
| Agitation Speed | 200 - 400 rpm |

The stirring rate was changed from 200 to 400 rpm in spite of the mode and the resins obtained were separated into the seven classes of the particle diameter. The fractions of the several classes of prepared resins at various stirring rate were represented in Table II.

The stirring rate of 200 rpm and 250 rpm, the particle size became smaller at the same rate by using unsteady speed impeller (Fig.1). Furthermore, by using unsteady speed mode, the rate of 250 rpm, the narrowest particle size distribution was obtained from 355~212 μm in 67 % fraction yield. Above 350 rpm, we could not detect any difference on the particle size and particle size distribution of the obtained resins between the two stirring mode. Microscope photographs of the resins

swelled in DMF prepared by using unsteady speed impeller at 250 rpm were shown in Fig.2. Fine spheres were observed at the several sizes.

Table II Particle size distribution of chloromethyl resin.

| Stirring mode and rate (rpm) | %Fraction of the recovered resin | | | | | | |
|------------------------------|----------------------------------|-----|-----|-----|-----|-----|-----|
| | (a) | (b) | (c) | (d) | (e) | (f) | (g) |
| Steady 200 | 61 | 23 | 7 | 1 | 0 | 0 | 0 |
| Steady 250 | 25 | 41 | 27 | 6 | 0 | 0 | 0 |
| Steady 300 | 4 | 18 | 59 | 8 | 2 | 0 | 0 |
| Steady 350 | 18 | 33 | 31 | 10 | 7 | 1 | 0 |
| Steady 400 | 3 | 9 | 42 | 20 | 18 | 2 | 0 |
| Unsteady 200 | 7 | 42 | 41 | 1 | 0 | 0 | 0 |
| Unsteady 250 | 1 | 3 | 67 | 20 | 6 | 0 | 0 |
| Unsteady 300 | 1 | 5 | 40 | 30 | 20 | 1 | 0 |
| Unsteady 350 | 4 | 15 | 41 | 20 | 15 | 2 | 0 |
| Unsteady 400 | 2 | 9 | 44 | 20 | 19 | 2 | 0 |

(a) $\sim 500 \mu\text{m}$, (b) 500~355 μm , (c) 355~212 μm , (d) 212~150 μm , (e) 150~75 μm , (f) 75~45 μm , (g) 45 μm ~.

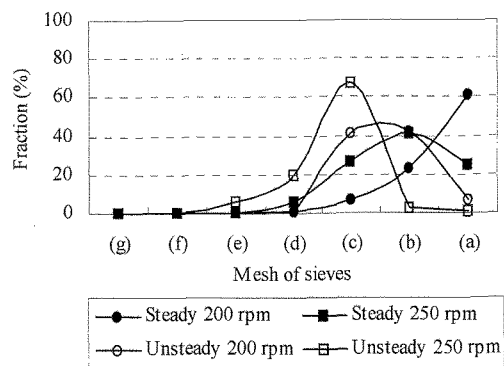


Fig.1 Particle size distribution of chloromethyl resin. (a) $\sim 500 \mu\text{m}$, (b) 500~355 μm , (c) 355~212 μm , (d) 212~150 μm , (e) 150~75 μm , (f) 75~45 μm , (g) 45 μm ~.

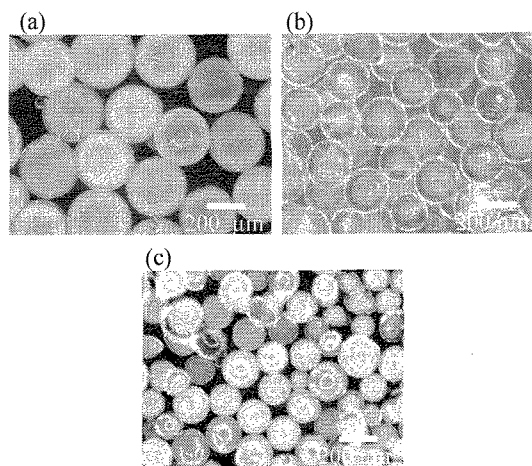


Fig.2 Digital microscope photographs of chloromethyl resin in DMF prepared by unsteady speed impeller at 250 rpm. (a) 500~355 μm , (b) 355~212 μm , (c) 212~150 μm .

3.2 Particle size distribution of polystyrene resin

The recipe for the conditions of the suspension polymerization was shown in Table III. The fractions

of the several classes of prepared resins at various stirring rate were shown in Table IV. By using steady speed impeller, the broad particle size distributions were observed for all the stirring rate. At 200 rpm by using unsteady speed mode, the narrowest particle size distribution was obtained from 500~355 μm in 55 % fraction yield. Above 250 rpm, we could not detect any difference on the particle size and particle size distribution of the obtained resins between the two stirring mode. Microscope photographs of the resins swelled in DMF prepared by using unsteady speed impeller at 200 rpm were shown in Fig.4. Fine spheres were observed at the several sizes.

Table III Recipe for preparation of polystyrene resin

| | |
|-----------------|---------------------|
| Water | 200 mL |
| Chlorobenzene | 11.4 mL |
| Styrene | 11.73 mL (0.10 mol) |
| DVB | 0.28mL (2.0 mmol) |
| BPO | 0.171 g (0.71 mmol) |
| Acacia gum | 8.0 g |
| NaCl | 5.0 g |
| Temperature | 85°C |
| Agitation Speed | 200 - 400 rpm |

Table IV Particle size distribution of polystyrene resin.

| Stirring mode and rate (rpm) | %Fraction of the recovered resin | | | | | | |
|------------------------------|----------------------------------|-----|-----|-----|-----|-----|-----|
| | (a) | (b) | (c) | (d) | (e) | (f) | (g) |
| Steady 200 | 67 | 22 | 4 | 0 | 0 | 0 | 0 |
| Steady 250 | 48 | 28 | 18 | 1 | 0 | 0 | 0 |
| Steady 300 | 39 | 33 | 27 | 0 | 0 | 0 | 0 |
| Steady 350 | 11 | 34 | 40 | 9 | 5 | 0 | 0 |
| Steady 400 | 5 | 13 | 26 | 15 | 32 | 4 | 0 |
| Unsteady 200 | 31 | 55 | 10 | 1 | 0 | 0 | 0 |
| Unsteady 250 | 32 | 28 | 25 | 9 | 5 | 0 | 0 |
| Unsteady 300 | 35 | 17 | 24 | 13 | 11 | 1 | 0 |
| Unsteady 350 | 6 | 18 | 45 | 17 | 11 | 1 | 0 |
| Unsteady 400 | 47 | 29 | 12 | 4 | 5 | 0 | 0 |

(a) ~500 μm , (b) 500~355 μm , (c) 355~212 μm , (d) 212~150 μm , (e) 150~75 μm , (f) 75~45 μm , (g) 45 μm ~.

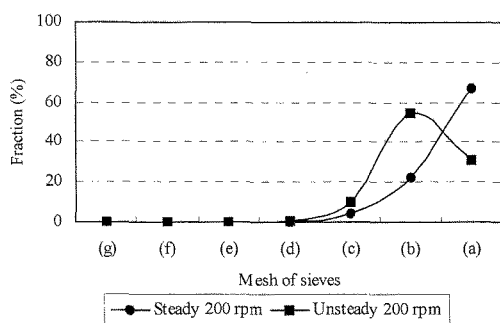


Fig.3 Particle size distribution of polystyrene resin. (a) ~500 μm , (b) 500~355 μm , (c) 355~212 μm , (d) 212~150 μm , (e) 150~75 μm , (f) 75~45 μm , (g) 45 μm ~.

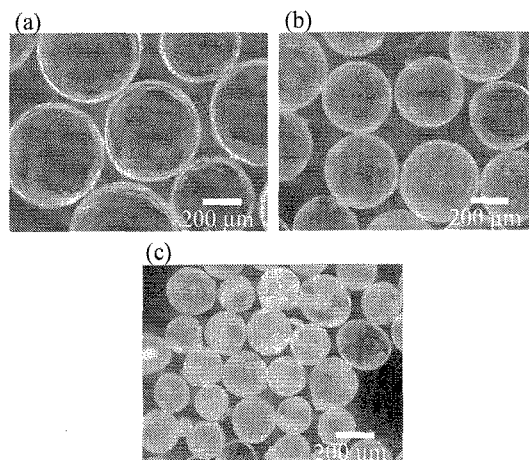


Fig.4 Digital microscope photographs of polystyrene resin in DMF prepared by unsteady speed impeller at 200 rpm. (a) 500~355 μm , (b) 355~212 μm , (c) 212~150 μm .

3.3 Particle size distribution of polystyrene resin using PVA and TCP

The recipe for the conditions of the suspension polymerization was shown in Table V. The fractions of the seven classes of prepared resins at various stirring rate were shown in Table VI. At 200 rpm by using unsteady speed mode, the narrowest particle size distribution was obtained from 355~212 μm in 80 % fraction yield. Above 250 rpm, we could not detect any difference on the particle size and particle size distribution of the obtained resins between the two stirring mode. The influence for the polymerization conditions of Table V and III, the particle size of resins in Table VI were bigger than that of Table IV except for 200 rpm of steady and unsteady speed modes. The viscosity of the organic phase in Table III might be lower than that of Table V. Microscope photographs of the resins swelled in DMF prepared by using unsteady speed impeller at 200 rpm were shown in Fig.6. Fine spheres were observed at the several sizes.

Table V Recipe for preparation of polystyrene resin

| | |
|-----------------|---------------------|
| Water | 200 mL |
| Styrene | 11.73 mL (0.10 mol) |
| DVB | 0.28mL (2.0 mmol) |
| BPO | 0.171 g (0.71 mmol) |
| PVA | 0.01 g |
| TCP | 0.10 g |
| Temperature | 85°C |
| Agitation Speed | 200 - 400 rpm |

Table VI Particle size distribution of polystyrene resin.

| Stirring mode and rate (rpm) | %Fraction of the recovered resin | | | | | | |
|------------------------------|----------------------------------|-----|-----|-----|-----|-----|-----|
| | (a) | (b) | (c) | (d) | (e) | (f) | (g) |
| Steady 200 | 6 | 39 | 50 | 3 | 1 | 0 | 0 |
| Steady 250 | 74 | 15 | 8 | 2 | 1 | 0 | 0 |
| Steady 300 | 71 | 17 | 7 | 2 | 4 | 0 | 0 |
| Steady 350 | 92 | 4 | 1 | 0 | 0 | 0 | 0 |
| Steady 400 | 29 | 49 | 19 | 1 | 0 | 0 | 0 |
| Unsteady 200 | 4 | 7 | 80 | 7 | 1 | 0 | 0 |
| Unsteady 250 | 65 | 17 | 12 | 4 | 1 | 0 | 0 |
| Unsteady 300 | 55 | 34 | 8 | 1 | 1 | 0 | 0 |
| Unsteady 350 | 90 | 7 | 2 | 0 | 0 | 0 | 0 |
| Unsteady 400 | 88 | 9 | 1 | 0 | 0 | 0 | 0 |

(a) ~500 μm , (b) 500~355 μm , (c) 355~212 μm , (d) 212~150 μm , (e) 150~75 μm , (f) 75~45 μm , (g) 45 μm ~.

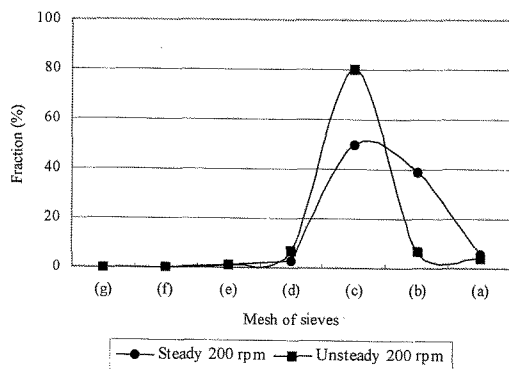


Fig.5 Particle size distribution of polystyrene resin. (a) ~500 μm , (b) 500~355 μm , (c) 355~212 μm , (d) 212~150 μm , (e) 150~75 μm , (f) 75~45 μm , (g) 45 μm ~.

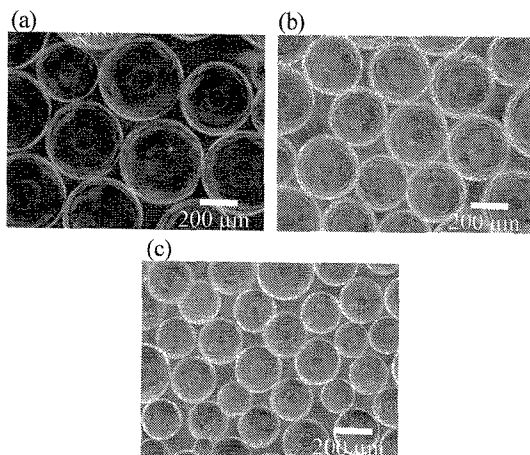


Fig.6 Digital microscope photographs of polystyrene resin in DMF prepared by unsteady speed impeller at 200 rpm. (a) 500~355 μm , (b) 355~212 μm , (c) 212~150 μm .

4. CONCLUSION

An effect of the use of unsteady speed impeller for suspension polymerization of cross-linked polystyrene resin was investigated. The preparations of the two types of resins, chloromethyl resin and polystyrene resin were examined by using acacia gum and NaCl as additives for aqueous phase. These results show the narrow particle

size distribution at 250 rpm for chloromethyl resin and 200 rpm for polystyrene. Furthermore the preparation of polystyrene resin by using PVA and TCP as additives shows the narrow particle size at 200 rpm. These results indicate that the unsteady speed impelling is a convenient and effective procedure to get a resin particles of narrow size. This method might be effective for the preparation of various polymers by suspension polymerization. The inference of the additives to the particle size of the resins prepared by suspension polymerization would be investigated further.

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